**Fig 1.0 Variation Of Compressive Strength with Water- Powder Ratio
(Predicted Equatio Curve & Orginal Values)**

- Compressive Strength of OPC at 28 days
- Compressive Strength of SCC at 28 days
- Predicted Compressive Strength of OPC at 28 days
- Predicted Compressive Strength of SCC at 28 days

Fig 2.0   Relationship between water/cement + Fly ash ratio (w/ (c+f) and 28 day cube strength

ALUMINA-SILICA RICH CLAY BRICK WASTE IN HYDROTHERMALLY TREATED CEMENT-BASED CONSTRUCTION PRODUCTS

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Abstract

An urgent need for creative, sustainable approaches, which minimise the environmental impact of conventional Portland Cement (PC) -based construction materials, is recognised throughout the world. In recent years intensive research has been directed to the use of alumino-silicate materials to produce blended PC. The reduction of CO_2 emissions, through the minimisation of PC consumption in the manufacture of PC-based construction products, and utilisation of industrial by-products, to limit environmental impact, are the principal drivers of this worldwide activity. A number of supplementary cementitious materials (SCMs) containing alumina and silica such as fly ash, granulated blast furnace slag and silica fume are well known additives for the production of blended PCs due to their pozzolanic properties. The potential of other by-products such as those from the construction and demolition industry are less known however, even though they represent an excellent source of reactive alumina and silica-rich material.

This paper deals with fired clay bricks (CB), generated as a waste product from construction and demolition activities, and their value as an additive in the manufacture of PC-based construction products. The research findings reported in this paper are from laboratory scale experiments conducted under hydrothermal conditions in an autoclave where finely ground CB waste was incorporated in the mixes. From a combination of analytical techniques including X-ray Diffraction, Differential Thermal Analysis, Scanning Electron Microscopy and solid-state Nuclear Magnetic Resonance, it was established that the aluminosilicate phase in the fired clay bricks promoted the development of the tobermorite, the principal binder in most calcium silicate products under hydrothermal conditions. The use of CB waste as a cement replacement for the manufacture of these products was also demonstrated as a viable option.

Introduction

The manufacture of Portland cement (PC), considered to be one of the most important and widely used construction materials for products such as concrete, consumes vast amount of both natural

resources and energy. As a consequence, the cement industry is amongst the largest single contributors to the greenhouse effect accounting for approximately 5% of the total global carbon dioxide emissions [1]. In order to address the issues of energy consumption and carbon dioxide emission, the utilisation of supplementary cementitious materials (SCMs) has been an important control measure directed at minimising the consumption of PC.

In recent years worldwide attention has been directed towards developing new technologies and methods for the utilization and recycling of industrial waste and by-products, such as fly ash [2], blast furnace slag [3] and silica fume, to produce blended PC and hence reduce PC consumption. Finely ground fired clay brick, an alumina-silica rich industrial waste generated from construction and demolition practices in many parts of the world, is a relatively new addition to the list of SCM. Recently the potential to incorporate CB waste as a SCM for the manufacture of autoclaved or hydrothermally cured calcium silicate based building products has been established [4, 5]. Previous studies have shown that CB exhibits pozzolonic characteristics and, therefore, it is feasible to partially replace cement with CB [6]. Although CB and OPC are compositionally compatible, being composed of the same main oxides, they are different in proportion and mineralogical composition; CB being rich in SiO_2 and Al_2O_3 and lean in CaO, whilst the opposite holds for OPC. These differences play an important role during the formation of the principal binder calcium silica hydrates (C-S-Hs)[1].

Millions of tonnes of fired clay-brick waste are generated worldwide each year, a large portion of which is destined for landfill. During manufacture, handling and transportation a large amount of fired-clay brick waste is generated. In addition, clay brick waste is generated from construction and demolition sites. Although some is recycled, a large amount ends up in landfills or reclamation sites for disposal.

A significant amount of research has been conducted into the potential reuse of such material, including as aggregate in the productions of paving blocks [7], unbound road sub-base [8], pozzolanic material [9] and natural sand replacement in autoclaved calcium silicate bricks [10]. Wild et al. [11] conducted research on the utilisation of waste clay brick and tile materials for the partial replacement of cement in concrete. Their comprehensive Copernicus Research Project, involving collaboration with four European partner institutions, produced promising results and demonstrated the feasibility of partial replacement of cement with ground fired clay brick in mortars and concrete.

Clay minerals, which are one of the principal ingredients in fired clay products, are essentially hydrous aluminosilicates, though magnesium and iron can substitute aluminium in varying degrees. Pozzolanic activity is not inherent to clay minerals but subject to high temperature heat treatment they can become 'active' [12, 13]; an example being the kaolinite-metakaolin transformation. Metakaolin is an ultrafine, pozzolanic material produced by the dehydroxylation of a kaolin precursor (natural alumina-silicate based mineral) upon heating at a temperature range of approximately 700° to 800°C. Metakaolin is essentially amorphous and it is in this disordered state that the silica and alumina present in its composition can fix calcium hydrate [14-16]. Under normal conditions at higher temperatures, typically involved in clay-brick production, recrystallisation resulting in the formation of new phases, takes place. With increased heating a spinel-type phase appears at 920°C having a topotactic relationship with metakaolin. At around 940°C microcrystalline mullite starts to form, the growth of which is enhanced as a result of the breakdown of the metakaolin structure providing amorphous free silica. At 1200°C the complete decomposition of the spinel-type phase is accomplished, prompting crystallisation of cristobalite from amorphous silica and the abrupt growth of mullite.

Hydrothermal curing or autoclaving is a proven and widely used process for the manufacture of cement based building products incorporating waste materials such as fly ash and blast furnace slag. Autoclaving enhances the reactivity of the raw starting materials due to the relatively high temperatures utilised. In the production of cement-based building products such as dense and aerated concretes, thermal insulation boards, and fibre-reinforced cement products, the technique provides several advantages over air curing including: the development within a few hours of permanent high early strength, a reduction in drying shrinkage, and a superior resistance to chemical attacks i.e. carbonation and sulphate attack [17].

One requirement when utilising Portland cement in an autoclave system is the enrichment of the mix with finely ground quartz sand (silica). Grinding of silica has two effects: it increases the materials specific surface area and it introduces energy into the surface layer; both of which enhance the reactivity of the silica. Furthermore, additional silica is required to ensure that the calcium silicate hydrate (C-S-H) and CH formed during the early stages of autoclaving will not combine to form α-C_2S hydrate. Though relatively dense α-C_2SH formation is undesirable as it crystallises as rectangular tablets and results in a final product that is porous and weak. Moreover, with larger additions of silica to the Portland cement, the formation of α-C_2SH avoided and a C-S-H of low Ca/Si ratio is formed (around 0.9 to 1.0) [18]; this C-S-H converts to tobermorite [19]. Tobermorite is regarded as one of the most important of the hydrous calcium silicate phases because it serves as the principal binder and provides the matrix strength associated with autoclaved calcium silicate based building products. As a consequence, extensive research has been conducted in optimizing the conversion of tobermorite from C-S-H over several decades [20-22]. It is well known that the rate of tobermorite formation in autoclaved FC products is accelerated by the presence of reactive Al-containing minerals and that Al substitutes for Si in tetrahedral sites in the tobermorite structure (Al-tobermorite) [23]. It is worthwhile to mention, that from the viewpoint of durability, Al-tobermorite is regarded more beneficial than Al-free tobermorite [24].

Research carried out on the industrially important CaO-Al_2O_3-SiO_2-H_2O system established a different reaction sequence for the formation of Al-tobermorite. In this context, previous research by Ray et al. [25] and Klimesch and Ray [26] at the University of Technology, Sydney, established that the use of reactive alumina-silica, such as metakaolin, in combination with Portland cement and silica were highly effective in the formation of Al-tobermorite.

Alumina-silica rich industrial wastes such as fired clay products (e.g. building bricks, pavers, tiles, etc.) are also reactive under autoclaving conditions and are available in large amounts many parts of the world as waste products. In Australia, this waste is currently taken to landfills at a cost of $40 per tonne. This paper reviews the results of investigations carried out at the University of Technology, Sydney, by the authors on hydrothermally cured quaternary blends comprised of PC, finely ground clay brick waste, reactive magnesia and quartz sand, based on 1:1 cement to quartz ratio. Recent work carried out by the authors has demonstrated that this alumina-silica rich waste when finely ground in combination with Portland cement and silica can be effective for the formation of highly crystalline Al-tobermorite after autoclaving at 180°C thus demonstrating that finely ground CB waste can be utilised as renewable construction materials.

Recent Research at the University of Technology, Sydney

Gutovic undertook a fundamental study of the suitability of clay-brick waste as a cement replacement in the hydrothermal environment [27]. OPC was replaced by four different finely

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[1] Cement chemists' notation is used throughout this document: A = Al_2O_3, C = CaO, H = H_2O, S = SiO_2 [1].

ground clay-brick types in combination with a quartz sand control at levels between 10 to 80 wt. %. The clay-brick represented had chemical compositions of SiO_2 between 53.36 and 71.82%, Al_2O_3 between 18.64 and 41.44%, and $CaCO_3$ content between 0.21 and 1.56%. Strength was found to increase with replacement of cement by clay-brick up to 40 to 50 wt. %, followed by a decrease at greater additions. Not surprisingly maximum strength corresponded to maximum amounts of highly crystalline tobermorite, the disappearance of lime-rich phases including portlandite and α-C_2SH, and a decrease in hydrogarnet amount. In addition high amounts of mullite and cristobalite along with low quartz content in the clay-brick corresponded to higher compressive strength. Whilst the major crystalline phases present in all brick types were quartz, mullite, haematite and cristobalite. The presence of mullite indicated the firing temperature was higher than those investigated by Wild et al. [11].

Connan [28] investigated the reactivity of the mullite phases and showed that whilst the clay-brick under investigation contained a large amount of Al_2O_3, only a minor quantity of the mullite phase was discernable. Using a combination of analytical techniques it was revealed that some quantity of the Al^{3+} present in the clay-brick was likely to be contained in a disordered glassy phase, hence accounting for its enhanced reactivity in comparison to synthetic mullite.

Further investigation by Connan of OPC-quartz mortar prepared with a cement to quartz ratio (40:60) comparable to commercially manufactured building products found that maximum strength, at 17.2 wt. % addition of clay-brick for silica, coincided with maximum tobermorite formation (Figure 1); other phases which formed included C-S-H, quartz, calcite and hydrogarnet. With continued replacement the amount of tobermorite decreased, and this along with other factors, clearly influenced a decrease in the strength. Scanning electron micrographs of the fractured surface of mortar cubes showed a variety of Al-tobermorite, the bulk being well crystalline lath-like structures.
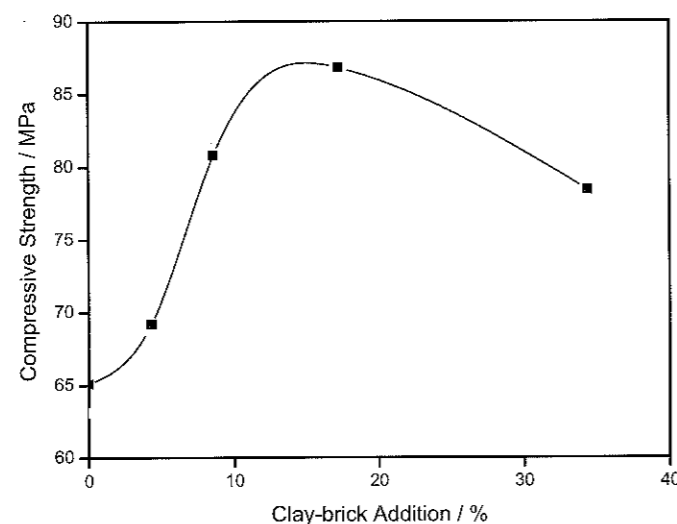

Figure 1 Compressive strength for OPC-quartz mortar cubes at various clay-brick additions.

The incorporation of Al into tobermorite was confirmed with DTA. From acid insoluble residue (AIR) data the increase in combined Al_2O_3 was mainly attributed to Al-tobermorite as the formation of the hydrogarnet phase ($C_3AlSi_{3-x}H_{2x}$ with x = 0 to 3) was minimal. The noted decrease in compressive strength was related to the increase in the Al/(Al+Si) ratio, hence promoting the formation of Al-(C-S-H) but decreasing the overall amount of Al-tobermorite formation. In relation to the reactivity of the aluminous source the combined Al_2O_3 was reduced from ~90% of the total Al_2O_3 for clay-brick free blends to ~40-45% at maximum addition. This

result, in combination with the amount of hydrogarnet formed, indicates that clay-brick is not as highly reactive an aluminous source as gibbsite under the hydrothermal conditions employed. The reactivity of the SiO_2 contained in the clay-brick fines was also shown to be greater than that of the ground quartz sand, of similar particle size distribution, which it replaced.

Liu et al. [29] studied the strength development of autoclaved OPC-quartz blends, where fired CB waste fines and reactive magnesia (MgO) partially replaced PC. Reactive MgO has been recognised as a potential additive to produce blended cement where its production, relative to PC, is less energy intensive thereby reducing CO_2 emissions. Three series of OPC mixtures were prepared using a constant 45:55 cement to quartz % mass ratio. The first series of mixtures is concerned with the addition of MgO (M series) at 5, 10, 15, and 20 mass % and the second series with the addition of CB (C series) waste at the same amounts. The third series dealt with the addition of both MgO and CB (CM series) in equal amounts having the total combined amount of 5, 10, 15, and 20 mass %. Compressive strength results for both C and CM series (Figure 2) showed an improvement in strength with increasing addition up to 15%. With increasing addition up to 20%, a relative decline in the strength was observed. The C20 (CB addition at 20 mass %) specimens showed approximately 6% reduction in strength, relative to the control, whilst the CM20 specimens maintained a strength gain of approximately 5%. The M series showed an overall decrease in strength with approximately 16% reduction at 20% addition. XRD and DTA analysis showed the presence of 1.1 nm Al-tobermorite in all specimens, in particular in blends containing CB waste. M series specimens showed a decrease in Al-tobermorite amounts, attributable to the decrease in the OPC amounts as more of the non-pozzolanic MgO is introduced to the system.
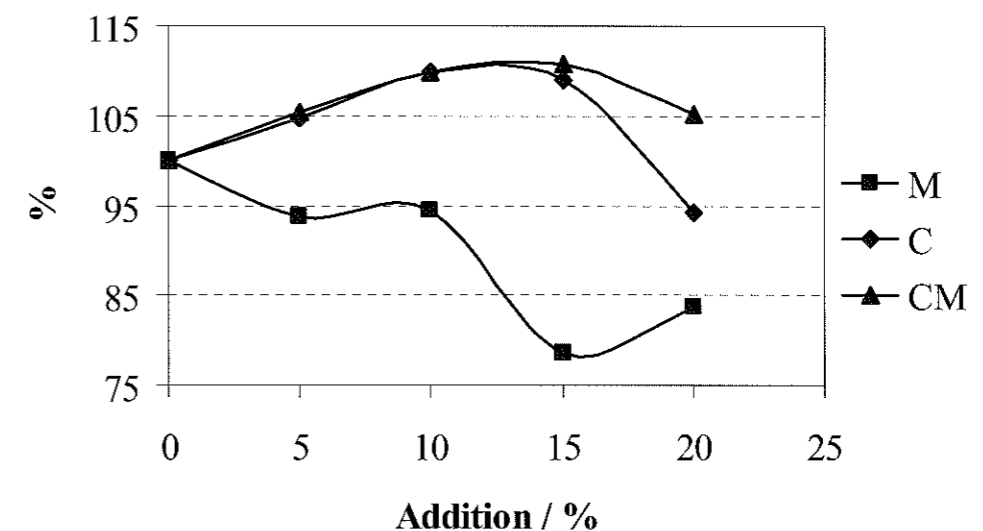

Figure 2 Normalised compressive strength as a function of MgO addition, clay-brick (CB) waste fines addition, and combined CB waste + MgO addition. The normalised data are calculated as a percentage relative to the control specimen (0% addition) for a particular autoclave run. Average compressive strength values of control specimens for: M series = 71.2 ± 4.6 MPa, C series = 73.4 ± 0.8 MPa and CM series = 71.2 ± 4.6 MPa. From Liu et al. [30].

The relationship between total bulk Al_2O_3 content in the starting raw mix and the beta-wollastonite (β-CS) formation temperature is depicted in Figure 3. The increase in Al-tobermorite is evident by the gradual reduction in height of the exothermic peak of the β-CS crystallisation

reaction accompanied by a progressive shift of this peak towards higher temperatures [30]. The C series showed a significant increase in the Al-tobermorite amounts whilst the CM series showed an overall reduction (from 845°C) in the exotherm temperature with an increase in the total Al_2O_3 content. Improved strength in CB added specimens were a result of the enhanced formation of C-S-Hs including tobermorite. The non-corresponding trends between strength and thermal data for the C and CM series suggested a possible suppression of the Al substitution reaction with the presence of MgO.
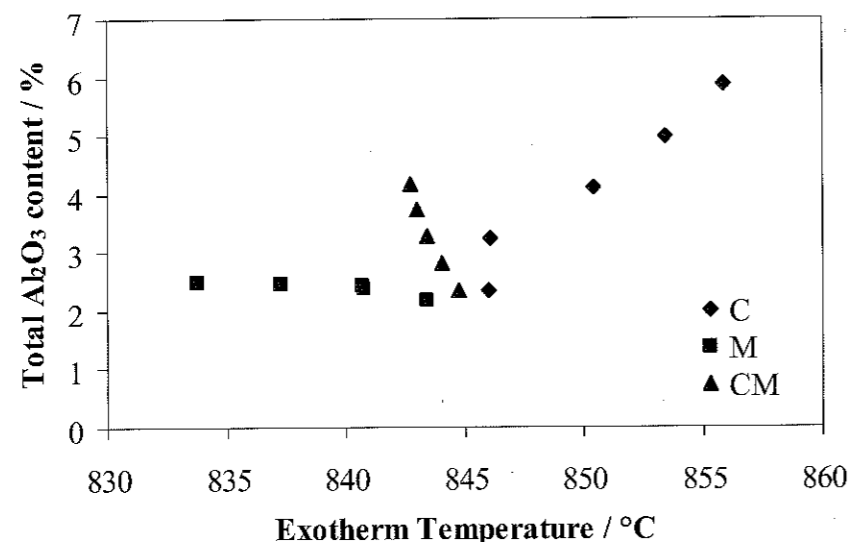

Figure 3 Total bulk Al_2O_3 content in the initial raw mix versus the variation in the β-CS formation temperature. From Liu et al. [30].

The authors suggested that the volume expansion of MgO to brucite has a physical effect in that it behaves as a filler producing more efficient packing leading to the retainment of strength across the CM-series. The presence of magnesite, from the partial carbonation of brucite, may also aid in packing. The physical interaction due to the volume expansion in CM series specimens is, therefore, likely to play an important role in controlling strength.

Conclusions
The phases formed at the completion of autoclaving depend largely on the starting raw materials used. Recent research by the authors at the University of Technology, Sydney, demonstrated that formation of 1.1nm tobermorite, regarded as the principal binder of most autoclaved calcium silicate based building materials, is enhanced by the addition of finely ground clay-brick to blends of OPC and quartz. Specifically, CB plays a significant role in the formations of tobermorite and hydrogarnet, which are critical phases in relation to both strength and durability. With the addition of MgO a possible retardation of the Al-tobermorite formation was observed in blends incorporating CB fines. However, the complementing physical and chemical effects from volume expansions of MgO may assist, at least partially, to produce more efficient packing.

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